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IS 1448-81 (1973): Methods of test for petroleum and its products, Part 81: Determination of trace elements in Petroleum products -- Total chlorine (wickbold oxyhydrogen combustion method) [PCD 1: Methods of Measurement and Test for Petroleum, Petroleum Products and Lubricants]

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Indian Standard

METHODS OF TEST FOR PETROLEUM AND ITS PRODUCTS: DETERMINATION OF TRACE ELEMENTS IN PETROLEUM PRODUCTS: TOTAL CHLORINE (WICKBOLD OXY-HYDROGEN COMBUSTION METHOD)

[P : 81]

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Adapted from IP 243/70T Sulphur in Petroleum Products Wickbold Oxy-hydrogen Method and IP 244/69T Chlorine in Petroleum Products Flask Combustion Method

1. SCOPE

1.1 This method describes a rapid procedure for the determination of trace amounts of chlorine in organic liquids. It is applicable to chlorine contents ranging from 0 to 500 ppm and is suitable for liquids in the volatility range up to and including gas oils.

NOTE — The method should not be used indiscriminately as other trace materials (for example, sulphur, bromine) may interfere.

2. OUTLINE OF THE METHOD

2.1 Depending on the chlorine content 5 to 100 g of sample is rapidly burnt in an oxy-hydrogen flame. The hydrochloric acid formed is absorbed in distilled water, converted to sodium chloride by addition of sodium hydroxide and titrated with standard mercuric nitrate solution, using diphenyl carbazone as indicator.

3. APPARATUS

3.1 Wickbold Combustion Apparatus — as shown schematically in Fig. 1.

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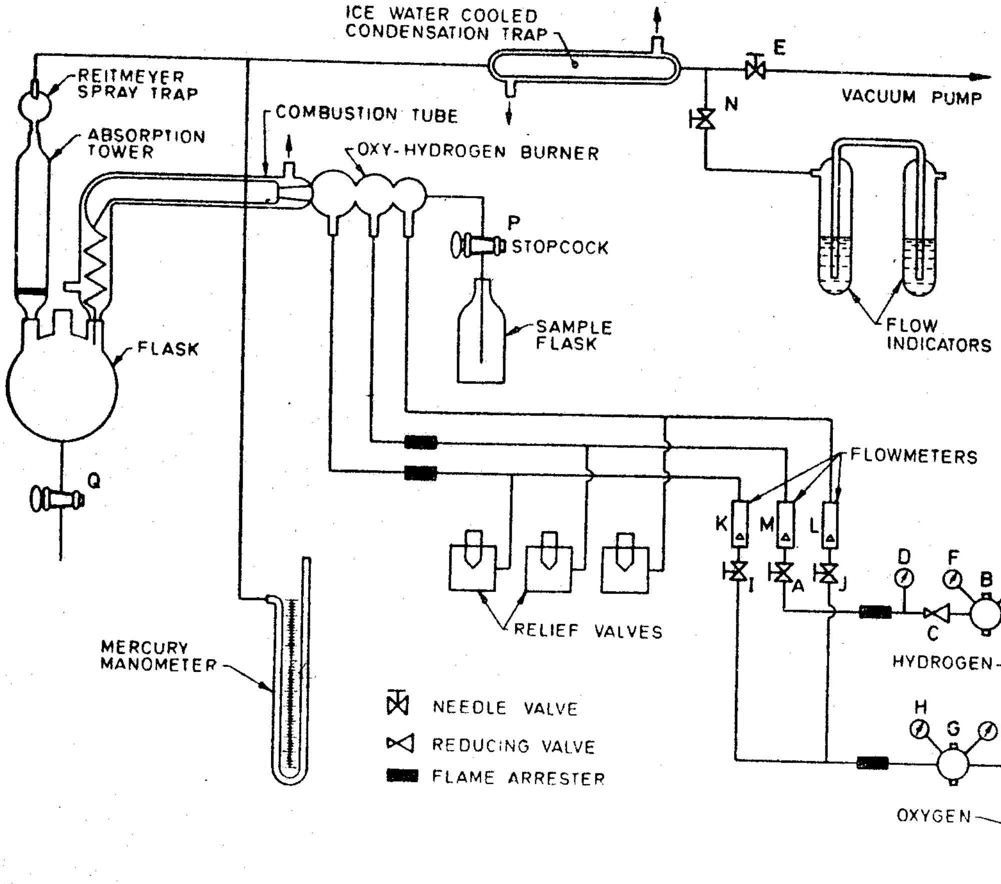

FIG. 1 WICKBOLD RAPID COMBUSTION APPARATUS FOR LIQUID SAMPLES OTHER THAN LPG

3.1.1 *Stand with Safety Shield* — The safety shield shall be made of colourless safety glass or its equivalent and mounted in front of and at the sides of the apparatus.

3.1.2 *Burner* — either quartz Wickbold burner or Fischer stainless-steel burner provided with inlets for primary oxygen, secondary oxygen, hydrogen, and the sample. (These burners will normally burn 5 to 6 ml of iso-octane per minute.) Flow diagrams are given in Fig. 2A and 2B.

3.1.3 *Combustion Tube with Condenser* — made of quartz.

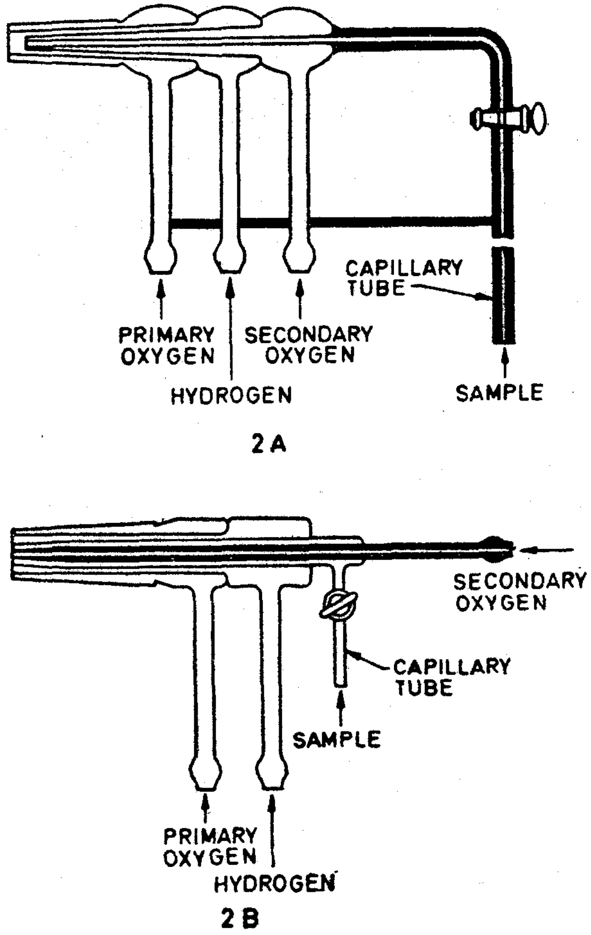

FIG. 2 ALTERNATIVE TYPES OF QUARTZ BURNER

3.1.4 *Flowmeter and Metal Control Valve for Primary Oxygen* — of safety design, and capable of measuring 1 000 litres per hour. A suitably calibrated mercury manometer is satisfactory.

3.1.5 *Flowmeter and Metal Control Valve for Secondary Oxygen* — of safety design, and capable of measuring 100 to 400 litres per hour. A suitably calibrated mercury differential manometer is satisfactory.

3.1.6 *Flowmeter and Metal Control Valve for Hydrogen* — of safety design, and capable of measuring 50 to 100 litres per hour of hydrogen.

3.1.7 *Mercury Manometer* — 400 mm in height, filled to a height of 200 mm and provided with a millimetre scale.

3.1.8 *Vacuum Needle Control Valves*

3.1.9 *Flask* — three-necked, 500 ml capacity, fitted with a stopcock.

3.1.10 *Absorption Tower* — provided with sintered filter plate (porosity 1) and cooling jacket.

3.1.11 *Reitmeyer Spray Trap*

3.1.12 *Metal Pressure Safety Valves* — for use in the primary and secondary oxygen lines and in the hydrogen line, 0·92 bar (0·9 atm) excess pressure.

3.1.13 *Flow Indicator* — made of glass.

3.2 Vacuum Pump — Capable of drawing at least 1 500 litres per hour through the apparatus, and protected by a water trap.

3.3 Oxygen Cylinder Reducing Head

3.4 Hydrogen Cylinder Reducing Head

3.5 Reducing Valve — for further reduction of hydrogen pressure from 3·45 to 0·345 bar.

3.6 Pressure Gauge — for measuring hydrogen pressure after final reduction.

3.7 Flame Arresters — of sheet fine mesh copper gauze, 650 mm^2 in area rolled to fit into the hydrogen and oxygen supply line in the position indicated in Fig. 1.

4. MATERIALS AND REAGENTS

4.0 Quality of the Reagents — Unless specified otherwise, pure chemicals and distilled water (*see* IS : 1070-1960*) shall be used in tests.

NOTE — 'Pure chemicals' shall mean chemicals that do not contain impurities which affect the results of analysis.

4.1 Hydrogen, Compressed

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*Specification for water, distilled quality (*revised*).

4.2 Oxygen, Compressed

4.3 Phenolphthalein Indicator Solution — 1 percent in 95 percent ethanol.

4.4 Sodium Hydroxide Solution — 2 percent (*m/v*), aqueous.

4.5 Solvent — free from chlorine, for example, iso-octane, ethanol or acetone.

4.6 Sodium Chloride Solution — 0·005 N. Dry sodium chloride for 2 hours at 105°C. Dissolve 0·292 2 g of dried sodium chloride in 500 ml of water and make up to 1 litre.

4.7 Mercuric Nitrate Solution — 0·005 N. Dissolve 0·86 g mercuric nitrate in 125 ml of 0·1 N nitric acid. Allow it to stand for 24 hours. Filter, if necessary, and make up to 1 litre with water. Standardize with 0·005 N sodium chloride by the procedure given in **6.13** and **6.14**. For titration take 5 ml of sodium chloride solution and dilute to 50 ml with water. Subtract a reagent blank determined in the same manner, omitting sodium chloride solution.

4.8 Barium Nitrate Solution — aqueous, 20 g/litre.

4.9 Diphenyl Carbazone Indicator Solution — 0·1 g/100 ml in ethyl alcohol (95 percent) or isopropyl alcohol.

4.10 Bromophenol Blue Indicator Solution — 0·05 g/100 ml in ethyl alcohol (95 percent) or isopropyl alcohol.

4.11 Nitric Acid — 0·1 N. Dilute 6·3 ml concentrated nitric acid (*see* IS : 264-1968*) (relative density 1·42) to 1 litre with water.

5. PREPARATION OF THE APPARATUS

5.1 Scrupulous cleanliness of sample containers and apparatus is required throughout. Glassware and quartzware should be cleaned with concentrated detergent but shall be finally thoroughly washed with water. More rigorous cleaning may be accomplished with dichromate-nitric acid cleaning agent. Quartzwares shall be cleaned by heating in a muffle furnace.

NOTE — It is preferable to reserve a set of sample containers, glassware, etc. for samples to be tested by this method.

5.2 Assemble the apparatus as shown in Fig. 1 and the gas supplies as in Fig. 2A or 2B. Use high pressure copper tubing to connect the oxygen and hydrogen supply to the control valves *A*, *I*, and *J*. Fill both limbs of the flow indicator with water to a height of approximately 30 mm. Suspend the burner from a piece of wire of such length as to permit easy manipulation.

CAUTION ! Ensure that the safety shield is in position.

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*Specification for nitric acid (*first revision*).

5.3 Close the oxygen and hydrogen control valves *A*, *I*, and *J*. Adjust the reducing head valve *B* of the hydrogen cylinder until the gauge *F*, shows a pressure of 3·45 bar. Now adjust the hydrogen control valve *C* until the pressure gauge *D* shows a pressure of 0·345 bar. Adjust the oxygen reducing head valve, *G* until the gauge *H* shows a pressure of 0·69 bar. Pass a rapid stream of water through the condenser and absorption tower, and iced water through the condensation trap. Close valve *E* and switch on the vacuum pump.

6. PROCEDURE

6.1 Select the appropriate sample size from Table 1 and weigh in a narrow-mouthed bottle of adequate size provided with an approximate volumetric division.

NOTE — If necessary for smooth combustion, the sample may be diluted with a known volume of a suitable solvent given in **4.5**.

TABLE 1 SAMPLE SIZE

CHLORINE RANGE (1)	MASS OF SAMPLE (2)	WEIGH TO THE NEAREST GRAM (3)
ppm	g	
0 to 20	100	0·5
20 „ 50	50	0·2
50 „ 100	25	0·05
100 „ 250	10	0·05
250 „ 500	5	0·01

6.2 Weigh the required amount of sample in a suitable bottle and quickly close it.

6.3 Insert the burner, close the burner stopcock *P*, and open the indicator stopcock *N*.

NOTE — It is imperative to take extreme care to wear safety goggles during the combustion stage.

6.4 Pass primary oxygen through the apparatus at a rate of 16 litres per minute and secondary oxygen at a rate of approximately 3 litres per minute at the same time opening the vacuum control value *E* until flow through the flow indicator stops. Then close stopcock *N* and adjust the vacuum control valve *E* to obtain a pressure of 26·7±6·7 mbar (20±5 mmHg) below atmospheric in the three-necked flask as indicated by the manometer.

6.5 Remove the spray trap from the absorption column and hold in one hand; with the other hand pour 50 ml of water into the absorber column. Replace the spray trap.

6.6 Take out the burner. Open the hydrogen valve *A* until a hydrogen flow rate of 0·8 litre per minute is achieved. Allow the hydrogen to pass for 30 seconds. Now ignite the hydrogen with a flint or battery-operated lighter or wax taper (do not use matches). Place the burner in the combustion tube taking care that the flame does not touch the wall of the standard joint. The pressure as measured by the manometer will now drop. Restore the pressure to approximately 26·7 mbar (20 mmHg) below atmospheric by manipulating the vacuum control valve *E*.

CAUTION ! Keep the burner mouth well away from the condenser opening during the 30 second flushing with hydrogen so as to prevent an explosive mixture of oxygen and hydrogen from entering the condenser.

6.7 Bring the sample in position, taking care that the sample inlet of the burner nearly reaches the bottom of the bottle.

6.8 Start the combustion by partially opening the burner stopcock *P*. Adjust the flame length using the burner stopcock *P* until the flame is approximately three-quarters of the length of combustion tube (*see* CAUTION). Start the stopcock. If the burner stopcock *P* is fully open further adjustment may be made using the vacuum control valve *E*.

CAUTION ! Should the burner flame extinguish at any time, first turn off the hydrogen at valve *A* turn off the sample supply at source, remove the burner and then quickly turn off the oxygen at valve *G*. Abandon the determination and prepare the apparatus for another determination as described in **5**.

NOTE 1 — If a sample shows poor combustion, read the pressure on the manometer. Improve combustion by increasing the secondary oxygen flow rate and restore the pressure on the manometer by manipulating the vacuum control valve *E*.

NOTE 2 — The occurrence of vapour bubbles between stopcock *P* and the burner indicates that too much suction is applied for the particular type of sample. In such cases reduce the suction (valve *E*) and open stopcock *P* wider to restore sample feed rate.

6.9 When the sample has been burnt, wash the sample bottle with three successive 2 ml portions of iso-octane or diluent solvent as appropriate. Allow each portion to burn, keeping the sample inlet filled all the time. Remove the sample bottle and gradually open the burner stopcock until the burner is emptied by suction taking care to maintain a slight vacuum in the three-necked flask. Close the burner stopcock *P*.

6.10 Restore the pressure in the three-necked flask to approximately 26·7 mbar (20 mmHg) below atmospheric and close the hydrogen valve *A*. Allow the burner to remain in place until the flame is extinguished. Stop the stopcock. Take the burner out of the combustion tube, close the oxygen valves *I* and *J* and the vacuum control valve *E*. Open the flow control indicator stopcock *N*. Switch off the vacuum pump. Lift the spray trap and allow the absorber solution to drain into the receiving flask. Remove the adaptor from the central neck of the flask.

6.11 Rinse the condenser, the splash bulb and the absorber abundantly with water, collecting the washings in the three-necked flask. Transfer the liquid quantitatively to a 500-ml conical flask and add 1 drop of phenolphthalein indicator solution. Make the solution slightly alkaline by dropwise addition of 2 percent sodium hydroxide solution. Evaporate the solution to a volume of approximately 50 ml and transfer it to a 100-ml volumetric flask. Wash the conical flask with water and transfer the washings to make the volume of solution to 100 ml.

6.12 Pipette 50 ml of the solution into a conical flask. Add 2 or 3 drops of bromophenol blue and 1 ml of barium nitrate solution (*see* Note 1). Neutralize the solution with 0·1 N nitric acid to a yellow colour and add 0·5 ml excess (*see* Note 2).

NOTE 1 — Barium nitrate solution is added to precipitate any sulphur present as barium sulphate, because sulphur interferes with the titration. The addition of 1 ml of barium nitrate may be omitted if no sulphur is present or may be increased, if found insufficient.

NOTE 2 — The prescribed acidification provides a satisfactory *p*H range of 3·0 to 3·5.

6.13 Add 0·5 ml (approximately 10 drops) of diphenyl carbazone indicator and titrate slowly with standard mercuric nitrate solution using a microburette, until a definite pink end point is obtained. Record the volume to nearest 0·01 ml.

6.14 Blank Determination

6.14.1 Make a blank determination by running the apparatus for an appropriate time with the oxy-hydrogen flame, and including in the combustion the same amount of diluent as used during the sample combustion procedure.

6.14.2 Apply the same titration procedure as used in the actual determination.

6.14.3 Redetermine the blank whenever new reagents are used.

7. CALCULATION AND REPORTING

7.1 Calculate the chlorine content from the following equation:

$$\text{Total chlorine, ppm} = \frac{(V_1 - V_2) \times N \times 71\,000}{M}$$

where

V_1 = volume in ml of standard mercuric nitrate solution required for the sample,

V_2 = volume in ml of standard mercuric nitrate solution required for the blank,

N = normality of the standard mercuric nitrate solution, and

M = mass in g of sample burnt.

7.2 Report the result as chlorine content, ppm.

8. PRECISION

8.1 Results of the duplicate tests shall not differ by more than the following amounts :

Repeatability	*Reproducibility*
$60/M$	Not yet established

where M = mass in g of the sample.

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